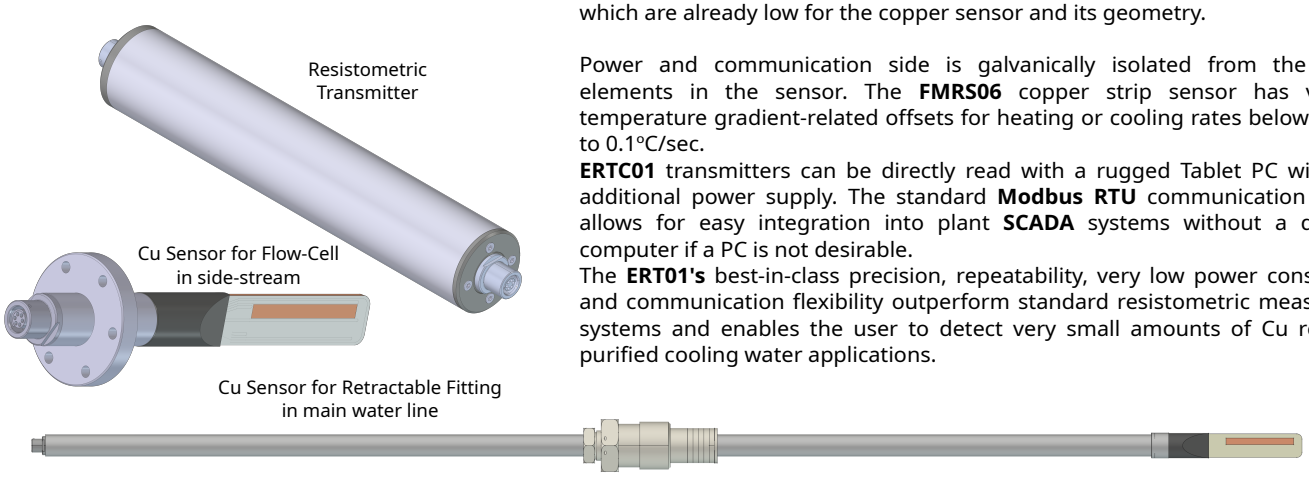
Resistometric Measurment System to Detect Copper Release in Purified Cooling Water Systems

FEATURES

- An 18-bit measuring resolution enables detection of a monolayer of Cu metal release from one-tenth of the exposed element surface.
- 2 Channel PSD detector for high error signal attenuation.
- Simultaneous Temperature measurement (-20ºC - 150ºC).
- Not compromized by conductive corrosion product films like CuO, Cu2O, CuS.
- Very low temperature drift for the measurement electronics (0.001% of FS from -10ºC to 70ºC).
- Supply current is very low. It draws 4.3mA at a 24 VDC supply voltage.
- Galvanically isolated sensor from supply and communication.
- RS485 Modbus RTU output for easy integration into SCADA systems, data loggers, radios and PLCs.
- O-ring sealed enclosure.
- Small size and weight.
- Energy flows in and out of the device are restricted to ensure use in hazardous areas.
- Resistance ratio or exposed element thickness output.

APPLICATIONS

- **Online Cu Release Monitoring in Cooling Water for Cu Hollow Conductors**
- **Corrosion Monitoring for Heat Exchangers**
- **Atmospheric Corrosion Monitoring**
- **Transformer Oil Monitoring**
- **General Cu Corrosion Testing**



DESCRIPTION

The **ERTC01** transmitter and copper sensor is specifically designed to detect copper release in cooling water systems used to cool hollow copper conductors. The **ERTC01** transmitter's operating principle is based on the resistometric technique outlined in the copper sensor data sheet **DS FMRS06**. A three-channel PSD detector is used for the **ERCT01** transmitter to detect metal release and temperature from a strip-shaped sensor element. Additionally a basic AI algorithm based on linear regression further improves the accuracy and precision of the collected ratio-metric measurement samples which are converted to metal release in the acquisition software.

The **ERTC01** transmitter uses Solenics-type strip-shaped copper metal elements as reference and sensing elements (resistors).
An internal reference element masked off from the exposed environment is used to compensate for the temperature-dependent resistance of the element material. The wall thickness for the exposed strip-type Solenics copper sensors is 0.0175 mm.

The **TCR** (Temperature Coefficient of Resistance) for the two elements (reference and exposed) is not exactly equal for the two elements in the sensor and also changes for the exposed element over its useful life span
(geometry change). Consequently, the resistance ratio also has a **TCR**. The sensor's ratio **TCR** is determined for each sensor after manufacturing. The calculated ratio **TCR**, along with the reference element temperature is used in the acquisition software to compensate for temperature-related offsets in the ratio value. The ratio **TCR** can be positive or negative and is in the range of <>±300 ppb/ºC for the copper sensor. For comparison, the **TCR** for copper is approximately 3000 ppm/ºC.

A low frequency (20 to 30 Hz) sinusoidal excitation signal drives the copper sensor to mask out thermal **EMF** and **Proximity**. The current through the in series connected elements induces eddy currents in the neighboring element (Proximity Effect). Consequently, the inductance of the elements increases. With rising temperature eddy currents decrease and the inductance decreases. The rise or fall in amplitude and phase shift is compensated for by synchronous demodulation, and only the real part of the element's signal is further processed. The low excitation frequency keeps the proximity signal at low levels which are already low for the copper sensor and its geometry.

Power and communication side is galvanically isolated from the sensing elements in the sensor. The **FMRS06** copper strip sensor has very low temperature gradient-related offsets for heating or cooling rates below or equal to 0.1ºC/sec.
ERTC01 transmitters can be directly read with a rugged Tablet PC without an additional power supply. The standard **Modbus RTU** communication protocol allows for easy integration into plant **SCADA** systems without a dedicated computer if a PC is not desirable.
The **ERT01's** best-in-class precision, repeatability, very low power consumption and communication flexibility outperform standard resistometric measurement systems and enables the user to detect very small amounts of Cu release in purified cooling water applications.

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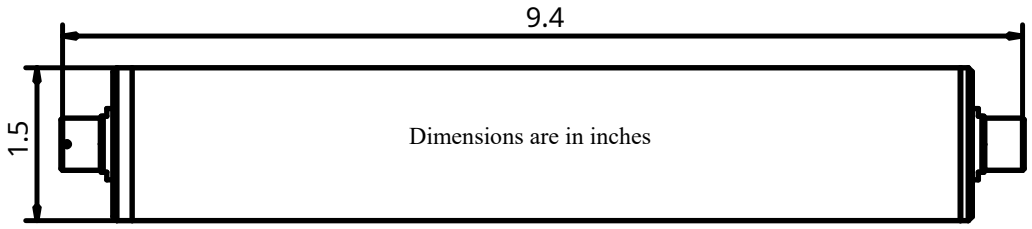
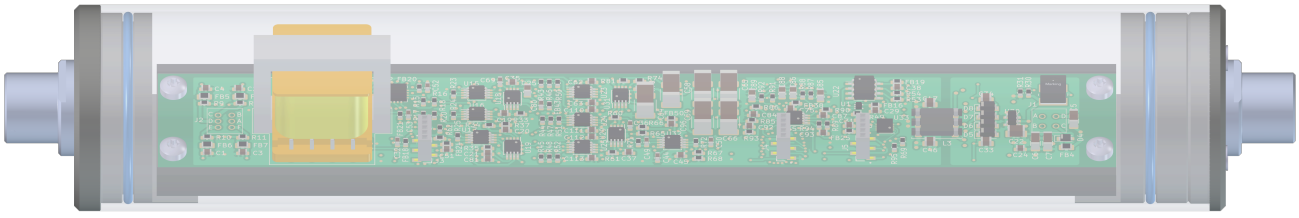
ERTC01 Transmitter Specifications

Enclosure	Stainless Steel with Fisher Connector entries.	For other enclosure options please contact SOLENICS
Connectors/Cables	6 pin Fischer connectors with 1 meter cable length max for the sensor.	For custom connections and cables please contact Solenics
Measurement Method	Ratio-metric Electrical Resistance	Modified Wheatstone Bridge
Signal Conditioning	3 Channel PSD	Phase Sensitive Demodulation
Resolution	18 bits	262144 points FS
Sensor Resistance Range	9.5 mohm for Copper	Transmitter can be adapted to other resistance ranges.
Channels	3	
Power Supply	6 to 36 VDC	
Current Consumption	3.8 mA at 24 VDC	
Communication	RS485 Solenics or Modbus RTU	For other Comm options please contact SOLENICS
Output Values	2	
Value 1	Sensor Ratio 0 to 262144 RRU	RRU = Resistance Ratio Units
Value2	Reference Element Temperature -20°C to 150°C	Circuit board body Temperature
Sensor Element Material	Copper	For other materials please contact SOLENICS
Sensitivity to thickness loss	**0.03 nm*** for 0.0175 mm wall thickness	
Precision	+/- 1 RRU for 9.5 mohm SR	Depends also on the rate of temperature change in the exposed environment.
Transmitter Temperature Drift	0.001% of FS from -10 to 70 °C	
Permanent Operating Temperature Range	-20 to 70 °C	
Excitation Output	28 Hz Sinusoidal	
Max Excitation Current	100mA	
Max Excitation Output Amplitude	40 mVpp	Terminal voltage for a disconnected sensor

*** 0.03 nm is not a monolayer of copper, and it means that if only one-tenth of the exposed copper surface releases a monolayer of copper the ratio increases by 1 RRU. 10 RRU represent approximately 1 monolayer of copper released from the exposed surface.**





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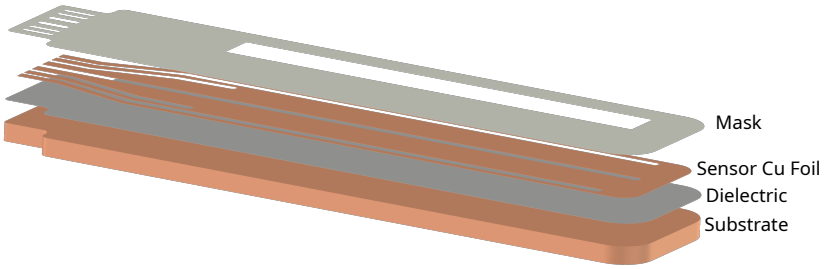
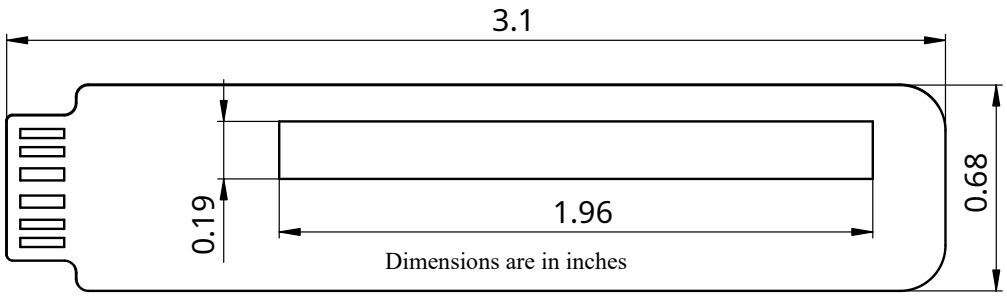
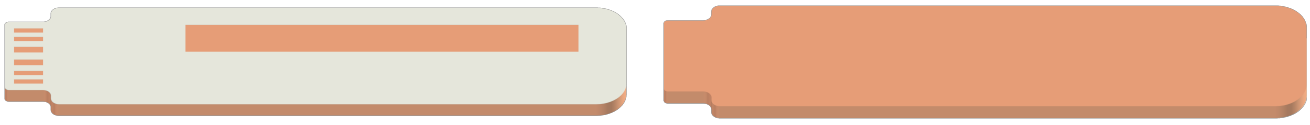
FMRS06 Strip Type Resistometric Copper Sensor Specifications

Detection Methode	Ratio-metric $R_{exposed}/R_{reference}$	
Sensor Strip Material	Copper Foil	For Cu grades please contact Solenics
Substrate Material	Copper	
Dielectric Material	High temperature epoxy/glass	
Mask Material	High temperature sulfur free epoxy	
Sensor Resistance	9.5 mohm	
Sensor Strip Thickness	0.0175 mm	
Effective Exposed Surface Area	240 mm^2	
Exitation Current	Maximum 100 mA Sinusoidal	
Permanent Operating Temperature	-20 °C to 120 °C maximum	
Maximum Operating Temperature	+150 °C	
Temperature Detection Methode	Resistance from reference element	







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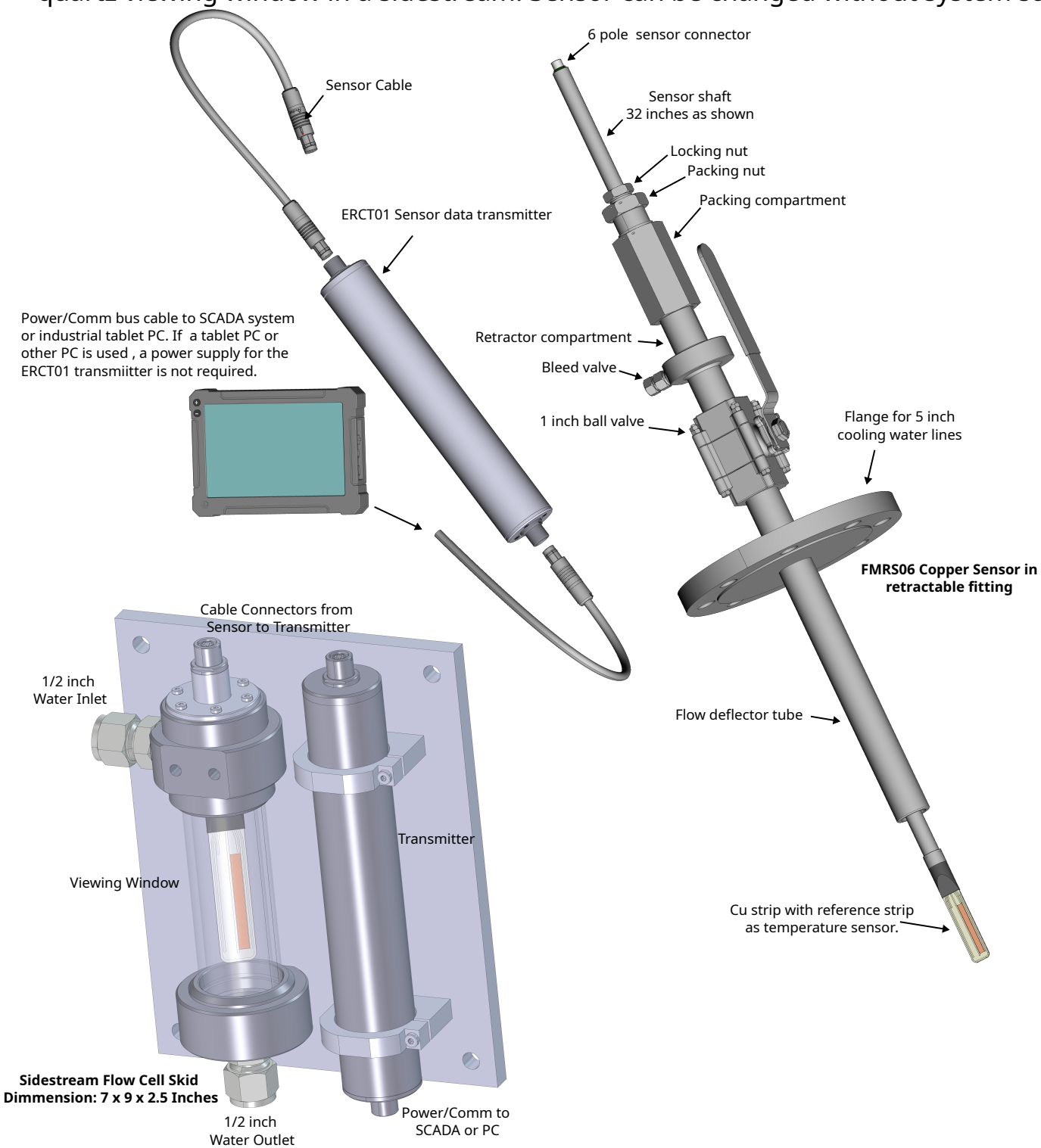
ERCT01 Transmitter with **FMRS06** Sensor in retractable access assembly or flow cell with quartz viewing window in a sidestream. Sensor can be changed without system sutdown.



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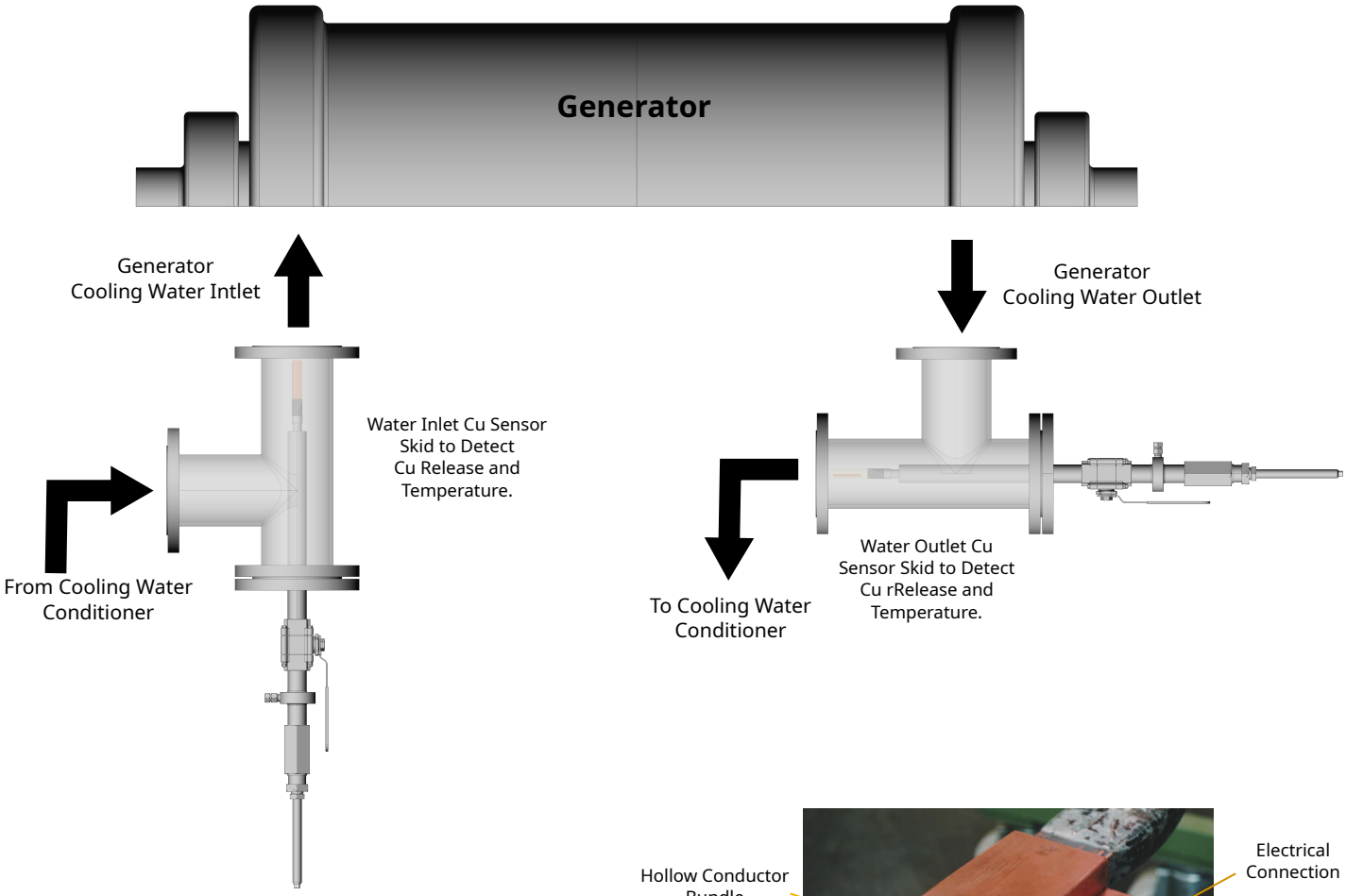
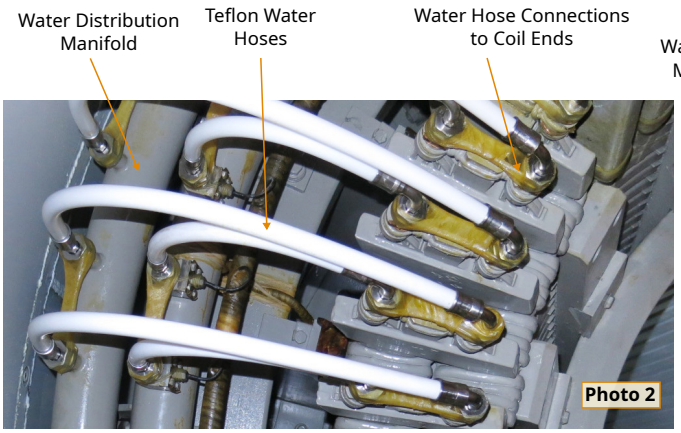
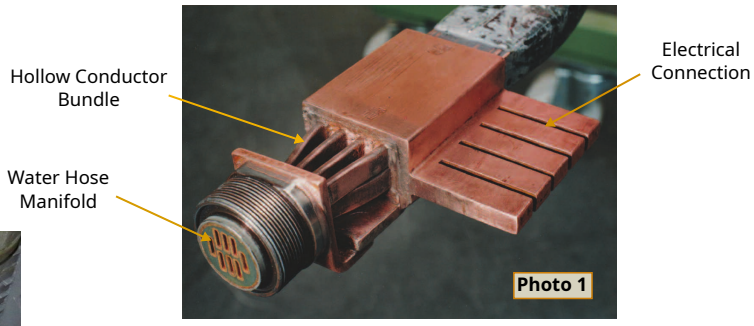
Inline arrangement with two retractable fittings for water inlet and water outlet monitoring. Recommended if line modifications are practicable.







Hollow conductor strand with water hose and electrical connection as used in a large generator.

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General Considerations Concerning Copper Release inside Hollow Conductors Cooled with Purified (DIW) Water.

Copper is subject to corrosive attack by aqueous solutions in turbulent flow. Pure water has minimal corrosive effect on a copper surface unless contaminants can enter the water in form of dissolved gases like O2, CO2 and pH moderators. In this case the effect of turbulent flow substantially enhances metal release from the copper surface and the factors influencing the corrosion rate are those which determine the amount of corrodents (O2) brought to the metal-liquid interface. To minimize Cu metal release rates, the velocity of the solution (water) in contact with the copper and the amount of dissolved oxygen should be held to the lowest value economically feasible. An acidic solution (water) and dissolved salts should also be avoided if possible.

Accompanying corrosion is the formation of a thin film of Cu2O and Cu (OH)2 on the metal surface which has a profound effect upon the Cu metal release rate.

The corrosion products, Cu20 and Cu (OH)2 tend to form a protective film on the surface of the copper, thus decreasing the rate of diffusion of oxygen to the surface.
Copper will not corrode appreciably in the absence of oxygen even in acid solutions. Any factor which increases diffusion of oxygen to the metal surface will increase the rate of corrosion. The rate of diffusion may be increased by either increasing the temperature, oxygen concentration in solution, by decreasing the thickness of the stagnant layer of liquid through which the oxygen must diffuse or by dissolving the protective oxide film. Since the amount of oxygen in solution is, according to Henry's Law, proportional to the partial pressure of oxygen above the solution, it may be controlled by bubbling various gases through the solution; i.e. either oxygen, air or nitrogen. Temperature decreases the amount of oxigen water can hold.

EFFECT OF VELOCITY
An increase in velocity has several effects upon corrosion. These are:

I.) Velocity reduces the thickness of the stagnant (laminar) layer of liquid next to the copper surface; hence, increasing the rate of diffusion of oxygen to the surface increases the corrosion rate.

2.) It hastens the removal of corrosion products and has an erosive effect upon any protective films, such as Cu2O or Cu(OH)2.
Both factors are favorable to a higher corrosion rate.

EFFECT OF pH
In general, protective films of copper oxide increase in stability with increasing pH.***** Thus, within limits, the more basic the solution, the more effective the film is in preventing oxygen diffusion.
Dissolved carbon dioxide (CO2) is an acid, and can neutralize and dissolve the film, thus increasing corrosion rate.

EFFECT OF Cu(OH)2
The compounds of copper(I) with oxygen and hydrogen are copper oxide (also known as cuprite Cu2O) and copper hydride, respectively. Cuprite is a stable and well known substance with regard to both its chemical and electrical properties. Copper hydride, on the other hand, is a less studied phase. It does exist, but it is very unstable and loses hydrogen quickly with time. It is also known that copper hydroxide Cu(OH)2 is a quite unstable species and is readily converted to Cu2O. Copper hydroxide may exist as a meta-stable phase, but its thermodynamic properties indicate that it is unstable compared with Cu2O and water. Copper hydroxide is the precursor of Cu2O and can be transported downstream in hollow conductors and redeposited at areas of turbulent flow where it accumulates as Cu2O or CuO which can cause plugging of hollow conductors over time.

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EFFECT OF TEMPERATURE

Temperature increases the rate of diffusion of oxygen in water, but it simultaneously decreases the amount of oxygen the water can hold.

Temperature significantly increases the diffusion rate of copper ions through copper oxide.

The relationship between temperature and diffusion follows the Arrhenius equation. As heat increases, the kinetic energy of the particles rises, which exponentially increases the diffusion coefficient of copper cations within the crystal lattice.

Enhanced Oxidation Rate:

Because the outward diffusion of copper ions drives the growth of the oxide film on the metal surface, higher temperatures directly accelerate the rate at which copper oxidizes.

Temperature generally accelerates the initial corrosion rate of copper in deionized water (DIW) by increasing reaction kinetics and ion mobility. However, in oxygen-bearing water, this relationship is complex because higher temperatures can decrease dissolved oxygen solubility, eventually forming protective oxide layers that inhibit further corrosion.

Accelerated Kinetics:

As defined by the Arrhenius equation, the thermal energy in the water raises reaction rates, accelerating both the cathodic (oxygen reduction) and anodic (copper oxidation) processes.

In hot pure water, copper rapidly reacts to form a layer of cuprous oxide (Cu2O) and cupric oxide (CuO), which strongly slows down the corrosion rate over time compared to the initial exposure.

Closed Systems:

In a closed system where oxygen cannot escape, the corrosion rate generally increases linearly with temperature if continously resupplied by leaks in the system.

Microbial Activity:

In less pure environments, moderate temperatures (around 25ºC to 45ºC) often spike copper degradation by providing the ideal environment for bacterial growth.

***** A major factor on the rate of corrosion is, in general rate of formation of protective films. Summarizing, the above mechanisms mentioned affect either the total solubility of oxygen, or its rate of diffusion to the metal surface.

EFFECT OF REDEPOSITION OF COPPER COMPOUNDS

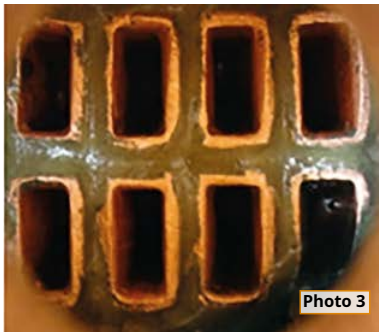
Photo 3

Photo 3 shows a clean or cleaned water hose manifold as also shown in Photo 1.

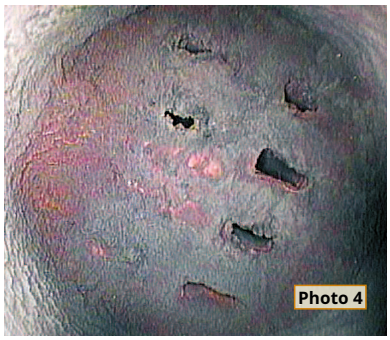
Photo 4

Photo 4 shows an oxide plugged water hose manifold. This is not copper corrosion, but rather what the evidence shows. The observed oxide deposits primarily result from the redeposition of Cu(OH)2 copper hydroxide which accumulated as Cu2O and CuO.

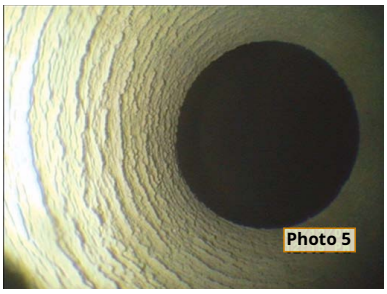
Photo 5

Photo 5 shows the inner surface of a Teflon water hose (as seen in Photo 2) coated with what analysis revealed to be Cu2O. This shows that non-negligible amounts of Cu were released inside the hollow copper conductors and into other areas of the cooling water system where it could be absorbed.

Electrical Resistance (ER) Versus Electrical Corrosion Potential (ECP) Measurments in Purified Cooling Water

Photos 4 and 5 indicate that Cu corrosion occurred somewhere inside the hollow conductors and evidence of it was redeposited throughout the cooling water system. To my knowledge, only electroanalytical methods are currently used to monitor the potential for Cu release from hollow copper conductors in generator cooling water systems.

Fig 1
ECP Sensor with
Reference Electrode

ECP

One of this methodes is to monitor the ECP (Electrical Corrosion Potential) with a three electrode arrangement like shown in **Fig 1**.
The ECP is not a direct measurement of metal release and cannot indicate if or how much metal is released from the copper surface. Instead, it measures the electrical state (mixed potential) of a metal's surface relative to its surrounding environment. It indicates whether the conditions are favorable for a metal to corrode or oxidize. It is highly dependent on factors like dissolved oxygen, hydrogen and several other factors in the water. The ECP cannot directly quantify Cu release.

ER

The ER (Electrical Resistance) technique is a well-proven method to detect metal release from an exposed metal's surface. Its principle relies on the fact that metal released from its exposed sensing element decreases the element's cross-section and consequently increases its electrical resistance. The relationship between resistance increase and exposed element thickness loss is used to calculate the metal release rate and, unlike the ECP method, is a direct measure for metal release.

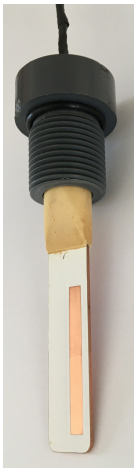

Fig 2
FMRS06 ER Sensor as used
in Test 1 & 2

For the proposed ER system, the sensitivity to metal release was substantially improved by minimizing cross-sensitivities to temperature and conductive deposits like Cu oxides.
The sensor's life span is 8 µm, meaning that after 8 µm of metal is released from its surface it has to be replaced.
The **FMRS06** ER sensor as shown in **Fig 2**, unlike ECP sensors, has no special operating requirements like calibration or electrolyte.
Its rugged construction permits use at high flow rates and elevated temperatures and pressures and guarantees a long service life.
The FMRS06 responsivness to upset cooling water conditions allow the operator to take action if required and it can also be a useful tool to monitor the total metal release during a hollow conductor cleaning operation.

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The following Cu metal release test in DIW water demonstrates the FMRS06 Cu sensors performance over temperature and its sensitivity to changing oxygen concentration or pH in DIW water.

Cu metal release test conditions for two separat tests : **Test 1** and **Test2**

DIW water is used in borosilicate glass jar as shown in **Fig. 1**.
The conductivity of the DIW water for both tests was < 2 uS throughout both test durations.
A mechanical stirrer provides agitation, as shown in **Fig. 1** for both tests during the test durations.
The glass jar is sealed with an o-ring sealed cap as shown in **Fig. 1**.
The glass jar is submerged into a mineral oil bath for cooling and heating as shown in **Fig. 2**.
Oxygen content was determined by Winkler analysis for the oxygenated water only.

Test 1
The oxygen concentration in the water is kept approximately at 2.5 mg/l throughout the test with a light vacuum above the water in the jar. Water temperature is increased and lowered as shown in the data graph. The pH for the water was slightly acidic, as it was from the storage container and was increased to pH 8 as indicated in the data graph.

Test 2
The oxygen concentration in the water is kept < 100 µg/l by continuously bubbling high-purity nitrogen. Water temperature is increased and lowered as shown in the data graph. The pH for this test remained slightly acidic throughout the test duration.

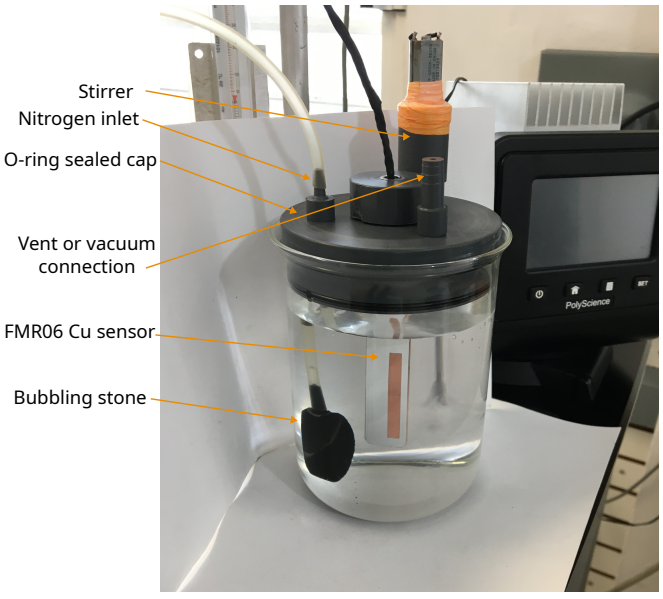

Fig. 1

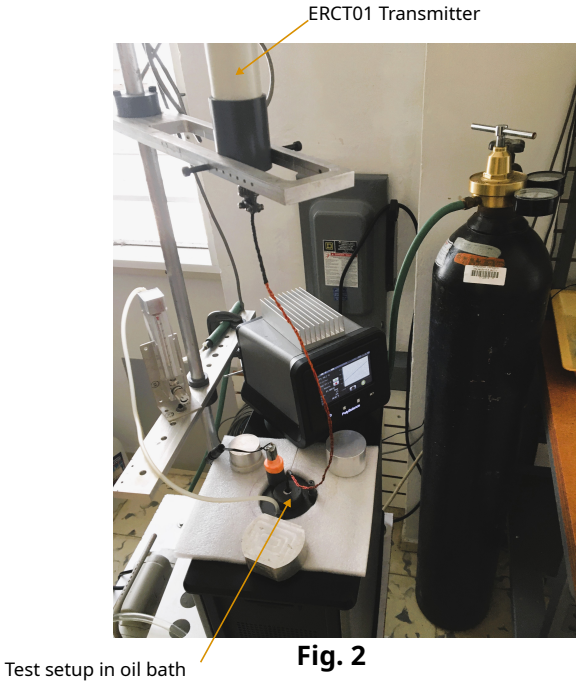

Fig. 2

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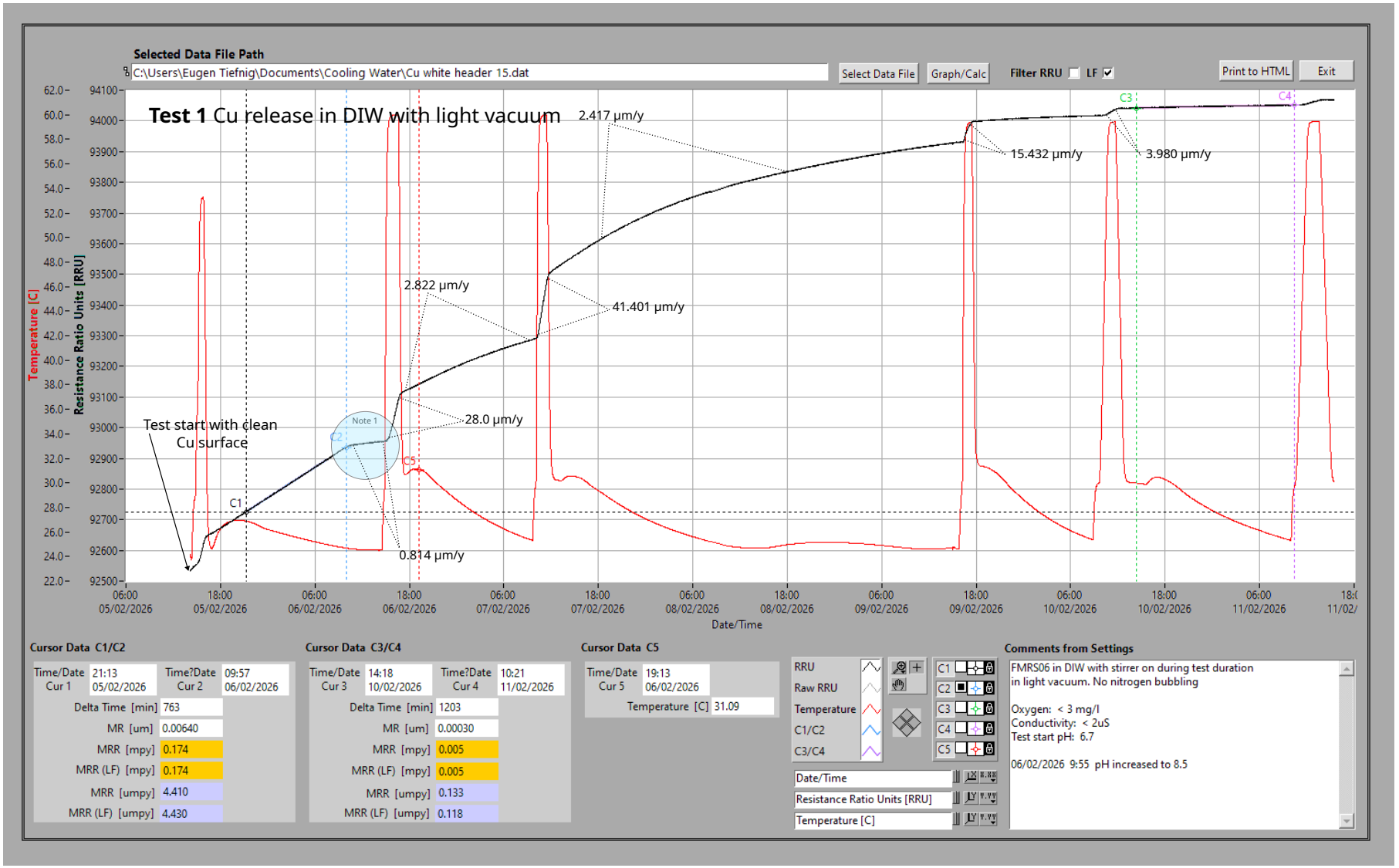

MR = Metal Release (Thickness Loss)
MRR = Metal Release Rate (Thickness Loss/Year)
MRR (LF) = Metal Release Rate (Linear Data Fit)
um = [µm]
umpy = [µm/year]
mpy = [mils/year]

Note 1:
pH was increased to 8 at the position of C2.
Metal release dropped sharply temporarily.

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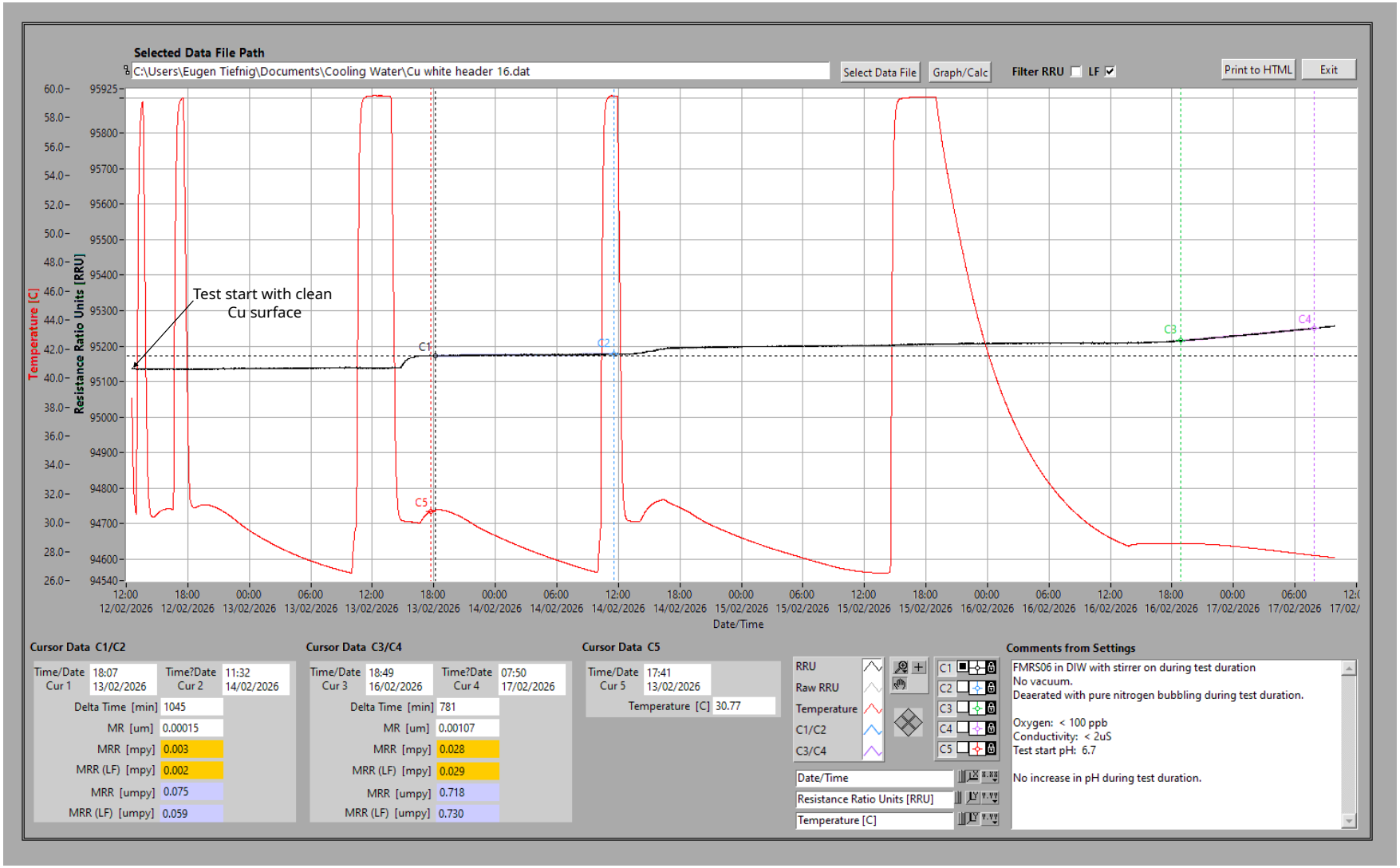

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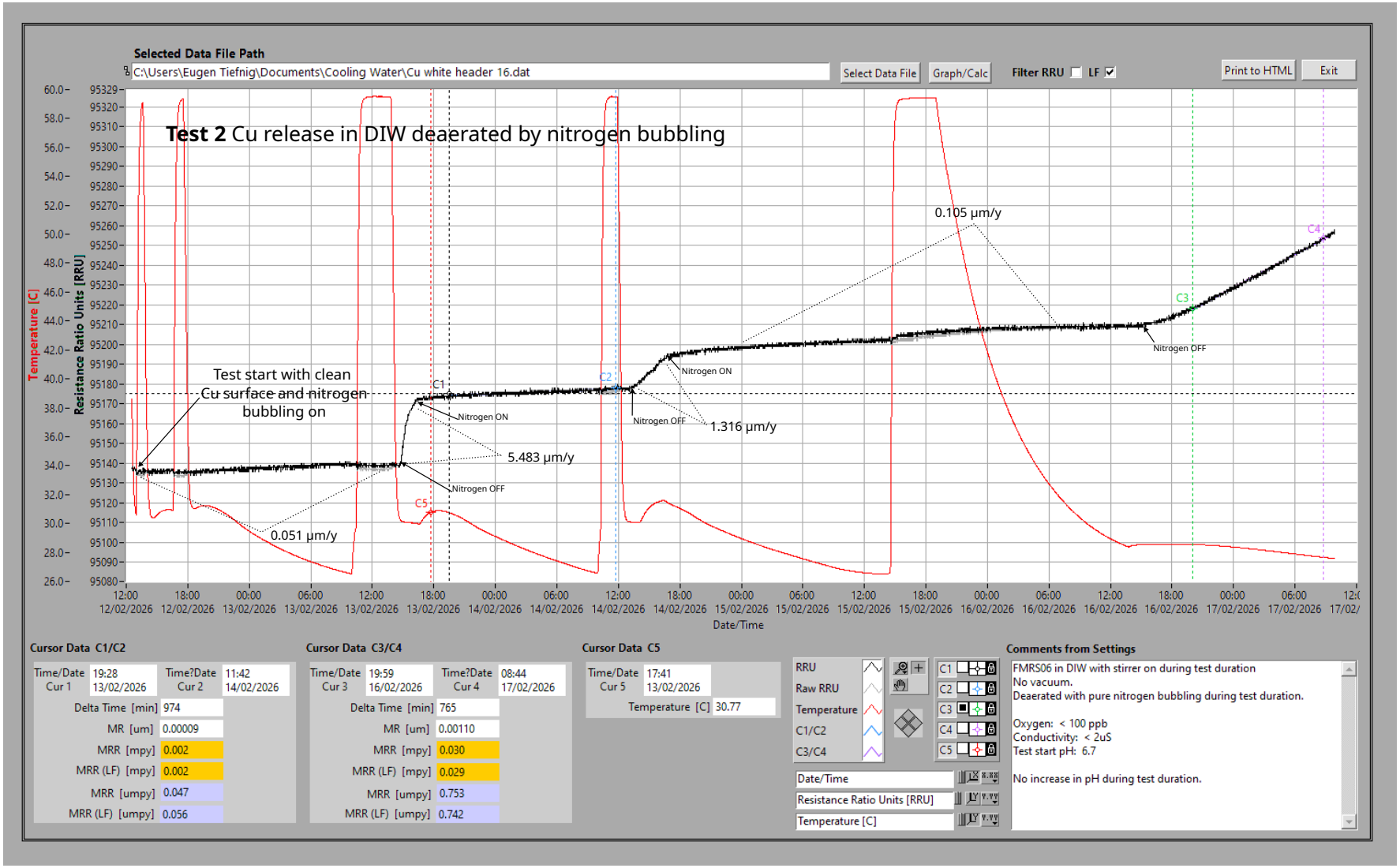

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Acknowledgments

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